

굴참나무 촉매열분해에 바이오매스 반탄화가 미치는 영향

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The Effect of Biomass Torrefaction on the Catalytic Pyrolysis of Korean Cork Oak

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초 록

본 연구에서는 굴참나무의 열분해 및 촉매 열분해에 바이오매스 반탄화가 미치는 영향에 대한 연구를 수행하였다. 굴참나무와 반탄화된 굴참나무의 열분해 및 촉매 열분해 거동은 열중량분석 결과와 회분식반응기를 이용한 급속열분해 반응에서 얻어진 바이오오일의 생성물분포를 비교하여 평가하였다. 굴참나무와 반탄화된 굴참나무의 열중량 곡선 및 미중열중량곡선은 굴참나무 내 헤미셀룰로오스의 제거량은 반탄화 온도 및 시간을 증가시킴에 따라 증가됨을 나타내었다. 굴참나무의 반탄화과정에서 헤미셀룰로오스의 제거로 굴참나무 내 셀룰로오스와 리그닌의 함량이 증가되기 때문에 열분해 과정에서 오일의 수율은 감소하고 고품질 수율은 증가하였다. 반탄화 굴참나무의 열분해 오일 중 레보글루코산과 페놀류의 선택도는 굴참나무 열분해 오일에 비해 높았다. 바이오오일 중 방향족 화합물의 함량은 HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) 상에서 굴참나무 및 반탄화된 굴참나무의 촉매열분해를 적용함으로써 증가되었다. 굴참나무에 비해, 반탄화 굴참나무는 HZSM-5를 이용한 촉매 열분해를 통한 방향족화합물 형성에 더 높은 효율을 보였고 더 높은 반탄화 온도(280 °C) 및 반응온도(600 °C)를 적용함으로써 극대화되었다.

Abstract

In this study, the effect of biomass torrefaction on the thermal and catalytic pyrolysis of cork oak was investigated. The thermal and catalytic pyrolysis behavior of cork oak (CO) and torrefied CO (TCO) were evaluated by comparing their thermogravimetric (TG) analysis results and product distributions of bio-oils obtained from the fast pyrolysis using a fixed bed reactor. TG and differential TG (DTG) curves of CO and TCO revealed that the elimination amount of hemicellulose in CO increased by applying the higher torrefaction temperature and longer torrefaction time. CO torrefaction also decreased the oil yield but increased that of solid char during the pyrolysis because the contents of cellulose and lignin in CO increased due to the elimination of hemicellulose during torrefaction. Selectivities of the levoglucosan and phenolics in TCO pyrolysis oil were higher than those in CO pyrolysis oil. The content of aromatic hydrocarbons in bio-oil increased by applying the catalytic pyrolysis of CO and TCO over HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$). Compared to CO, TCO showed the higher efficiency on the formation of aromatic hydrocarbons via the catalytic pyrolysis over HZSM-5 and the efficiency was maximized by applying the higher torrefaction and catalytic pyrolysis reaction temperatures of 280 and 600 °C, respectively.

Keywords: torrefaction, pyrolysis, HZSM-5, aromatic hydrocarbons

1. Introduction

During several decades, many researchers have investigated the conversion of biomass to mitigate the current issue related with energy shortage, environmental contamination, and climate change[1]. Lignocellulosic biomass is the only renewable carbon source which can re-

place fossil fuels and can be converted to value added chemicals via various kinds of conversion technology such as physical, biological, chemical and thermal treatments. Product quality on the biomass conversion is differentiated by its lignocellulosic composition and property[2,3].

Biomass pyrolysis is known as a proper method for the production of bio-oil because the amount of bio-oil can be maximized by applying medium high temperature, normally at between 400 and 600 °C, under non-oxygen atmosphere. However, the quality of biomass pyrolysis oil is still low because most of them is consisted with oxygen containing unstable chemicals and needs to be upgraded by applying catalytic process[4-6]. Although the amounts of stable hydrocarbons in the prod-

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Table 1. Physicochemical Properties of Zeolite Catalysts

Catalyst	HZSM-5 (CBV 3024E)
SiO ₂ /Al ₂ O ₃	30
Surface area (m ² /g)	405
Pore size (Å)	5.1 × 5.5, 5.3 × 5.6
Internal pore space (Å)	6.36
IZA code	MFI

uct bio-oil can be increased by applying catalytic process, the actual commercialization of product oil obtained from the catalytic pyrolysis of biomass is still limited due to the low yields of target products such as aromatic hydrocarbons.

Torrefaction is a simple thermal pretreatment method which allows heat at between 200 and 300 °C under non-oxygen atmosphere. Recently, biomass torrefaction was attempted to modify the structure of biomass to more proper feedstock on the pyrolysis and catalytic pyrolysis for the production of value increased bio-oil from biomass[2]. Meng et al.[7] torrefied loblolly pine to produce high quality oil with low water content during its pyrolysis. They indicate that the typical pyrolyzates of hemicellulose and cellulose were decreased with the increase of lignin pyrolyzates by the use of torrefied pine as the feedstock of pyrolysis. Sadaka et al.[8] applied different temperature and time for the torrefaction of biomass and found that the torrefaction temperature is the main factor on the structural modification of biomass via the torrefaction and pyrolysis of wheat straw, rice straw, and cotton gin waste.

Torrefaction was also used as a pretreatment method of biomass for the use on the catalytic pyrolysis. Many kinds of biomass, such as yellow poplar[9], pinewood[10,11], Eucalyptus globulus[12], cellulose [2,13], lignin[14,15], sewage sludge[16] were torrefied and applied on their catalytic pyrolysis to increase the yield of target hydrocarbons. Chen et al.[11] examined the catalytic pyrolysis of torrefied pinewood and produced high quality bio-oil having the higher heating value and aromatic hydrocarbons yield than that of untorrefied pinewood. They explained that the decreased oxygen content in torrefied biomass is the main reason for the improved quality produced from the catalytic pyrolysis of torrefied biomass. Mahadevan et al.[15] torrefied two kinds of organosolv lignin, extracted from pine and switchgrass, at different temperatures. They found that the torrefaction of lignin enhanced the aryl ether link cleavage, demethoxylation, demethoxylation, polycondensation of guaiacyl lignin. Compared to untorrefied lignins, torrefied lignins produced the larger amounts of phenols and solid residue from non-catalytic pyrolysis and increased the selectivity of aromatic hydrocarbons during their catalytic pyrolysis over HZSM-5. Adhikari et al.[14] also found that the higher efficiency on the elimination of oxygenates and formation of aromatic hydrocarbons can be achieved by applying the torrefied lignin as a feedstock on the catalytic pyrolysis over HZSM-5 having various SiO₂/Al₂O₃ ratios. Although the effect of biomass torrefaction on the thermal and catalytic pyrolysis of biomass was reported by many researchers, the study for the optimized torrefaction condition is still insufficient.

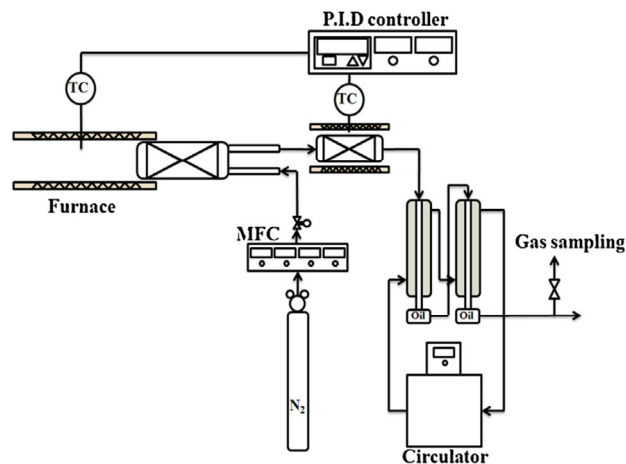


Figure 1. Schematic diagram of two stage fixed bed reactor[17].

Therefore, the effects of biomass torrefaction temperature and time on the thermal and catalytic pyrolysis of cork oak (CO) were estimated using a thermogravimetric (TG) analyzer and fixed-bed reactor in this study. HZSM-5 (30), SiO₂/Al₂O₃; 30, was used as the ex-situ catalyst on the catalytic pyrolysis using a fixed-bed reactor. Temperature and reaction time for the torrefaction of CO were varied to know the effect of torrefaction condition on the thermal and catalytic pyrolysis.

2. Materials and Methods

2.1. CO and its torrefaction

CO, Korean native oak tree, was cryo-milled, sieved, and dried at 105 °C for 8 hours to make the moisture free particles smaller than 1.0 mm. Four kinds of torrefied CO (TCO) were prepared by applying different torrefaction temperature (250 and 280 °C) and time (0.5 and 1.0 hour) under nitrogen atmosphere in a fixed-bed reactor (Figure 1) and assigned as TCO (250-0.5), TCO (250-1), TCO (280-0.5), and TCO (280-1), respectively. Physico-chemical and thermal properties of CO and TCOs were characterized by ultimate, proximate, and TG analysis.

2.2. Catalyst

A commercial microporous catalyst, HZSM-5(30) having SiO₂/Al₂O₃ = 30, was purchased from Zeolyst and calcined at 550 °C for 3 hours prior to the catalytic pyrolysis experiments. The physic-chemical property of HZSM-5(30) was shown in Table 1.

2.3. Ex-situ catalytic pyrolysis using a fixed bed reactor

Thermal and catalytic pyrolysis of CO and TCO were performed using a fixed bed reactor (Figure 1) which can control the temperature of 1st and 2nd furnace, independently. For the non-catalytic pyrolysis, 3 g of CO or TCO was loaded into 1st reactor and purged with nitrogen gas for 30 minutes. After purging time, the pyrolysis of biomass was initiated by sliding the preheated furnace at 530 °C. The product vapor emitted from the reactor was condensed in a liquid collector and uncondensed gas was collected using a Teflon bag. The product oil and

Table 2. Ultimate and Proximate Analysis

	C	H	N	O ^a	C/O	Moisture	Volatile matter	Fixed carbon	Ash
CO	48.5	5.9	0.3	45.3	1.07	2.5	82.2	14.6	0.7
TCO (250-0.5)	51.6	5.8	0.2	42.4	1.22	0.6	82.3	16.3	0.8
TCO (250-1)	51.9	5.7	0.2	42.2	1.23	0.5	79.8	18.9	0.8
TCO (280-0.5)	54.5	5.6	0.2	39.7	1.37	0.7	73.9	23.9	1.5
TCO (280-1)	55.1	5.6	0.2	39.1	1.41	0.4	71.6	26.5	1.5

^aBy difference.

gas were analyzed using a gas chromatography/mass spectrometry/flame ion detector/thermal conductivity detector (GC/MS/FID/TCD), respectively. The same experimental condition for GC/MS/FID/TCD used in our previous literature[17,18] was applied also in this study.

3. Results and Discussion

3.1. Physico-chemical properties of torrefied CO

Table 2 showed the proximate and ultimate analysis results of CO and TCOs. Compared to CO, TCO had the higher C/O ratio, indicating the decrease of elimination of oxygen in CO due to the torrefaction. The contents of fixed carbon and ash in TCOs were higher than those in CO. This indicates that the considerable amount of volatile matter was eliminated by the torrefaction. The decrease of oxygen and volatile matter by the torrefaction of CO can be explained by the decomposition of hemicellulose. Barta-Ranjnai et al.[19] indicated that the decomposition of hemicellulose and the partial change of cellulose and lignin can be achieved by the torrefaction of biomass. The increase of carbon and fixed carbon content in TCO also can be explained by the crosslinking and charring during its torrefaction. Zheng et al.[20] also reported the increased carbon and fixed carbon content in TCO because of the deoxygenation and charring caused by its torrefaction. Mahadevan et al.[15] also reported the increase of carbon, fixed carbon, and ash content via the torrefaction of lignin. In our experiments, total weight of CO were decreased to 84.7 wt% for TCO (250-0.5), 80.0 wt% for TCO (250-1), 71.9 wt% for TCO (280-0.5) and 69.0 wt% for TCO (280-1), respectively. This also indicated that the considerable amounts of CO, up to 31.0 wt% of initial mass, were eliminated by applying torrefaction. This can confirm that considerable amount of biomass component in CO is eliminated by its torrefaction and this elimination extent was increased by applying the higher temperature and longer time for the torrefaction.

Figure 2 shows the TG and differential TG (DTG) curves of CO and TCOs obtained from their TG analysis at 30 °C/min. Main components of woody biomass decomposed at different temperature regions, 200-350 °C for hemicellulose, 350-400 °C for cellulose, and 200-600 °C for lignin, respectively. Therefore, the left shoulder peak, main peak, and right tailing peak on the DTG curve of CO, Figure 2(b), can be assigned as the decomposition of hemicellulose, cellulose, and lignin in CO. As shown in Figure 2(b), the peak height of left shoulder peak on the DTG curves of TCOs was gradually decreased by increasing the

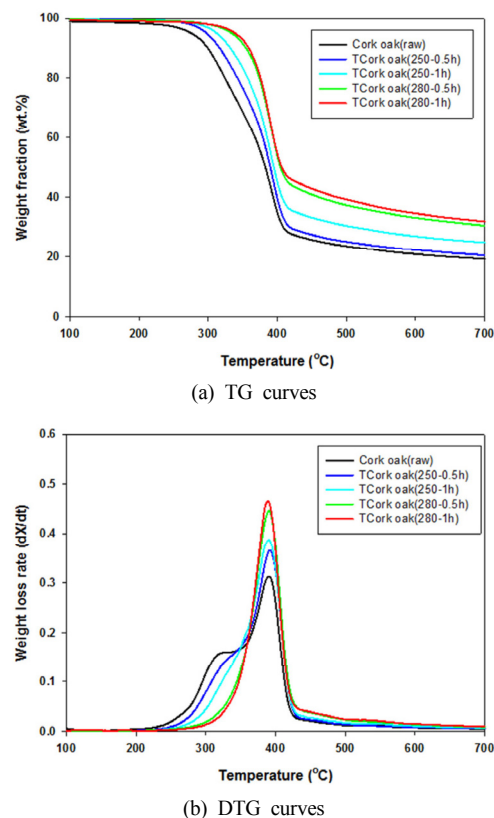


Figure 2. TG and DTG curves of raw and torrefied cork oak.

torrefaction temperature and time. This can explain that hemicellulose is mainly eliminated during the torrefaction of biomass and maximized by increasing torrefaction temperature and time. Zheng et al.[21] also found the elimination extent of hemicellulose in biomass can be increased due to the increase of torrefaction severity.

3.2. Non-catalytic pyrolysis of CO and TCOs

Figure 3 shows the yields of gas, oil, and char obtained from the non-catalytic pyrolysis of CO and TCOs at 530 °C in a fixed bed reactor. The yield of char was increased together with the decrease of oil by applying CO torrefaction. This tendency was increased by allowing the higher temperature and longer torrefaction time. The decrease of oil and increase of char in TCO can be explained by the decrease of hemicellulose and increase of lignin contents due to the elimination of hemicellulose during the torrefaction. Among lignocellulosic compo-

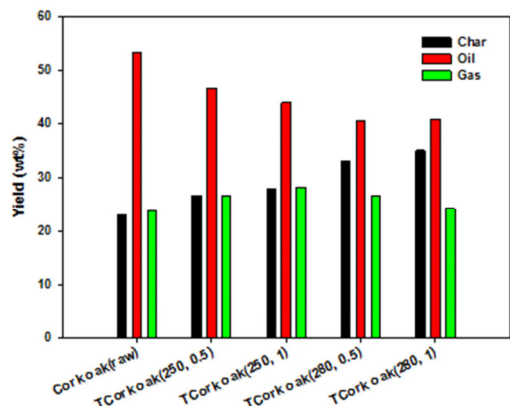


Figure 3. The yields of gas, oil, and char obtained from the non-catalytic pyrolysis of CO and TCOs at 530 °C.

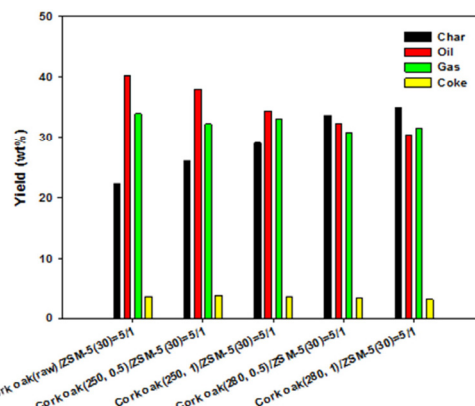
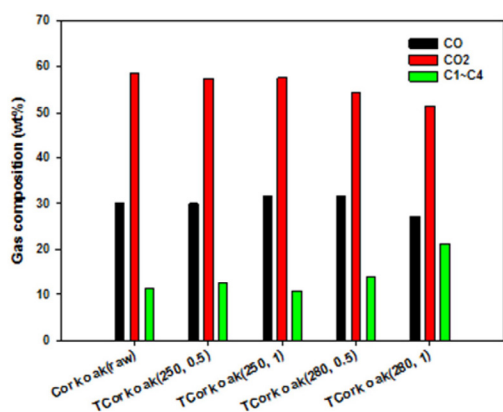
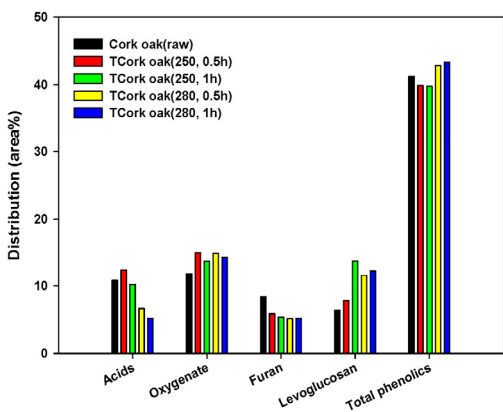


Figure 5. The yields of gas, oil, char, and coke obtained from the catalytic pyrolysis of CO and TCOs over HZSM-5 at 530 °C.



(a) Gas



(b) Oil

Figure 4. Product distribution of gas and oil obtained from the non-catalytic pyrolysis of CO and TCOs at 530 °C.

nents of woody biomass, lignin produces the largest amount of solid char during its pyrolysis due to the structural stability of lignin[17].

The gas composition obtained from the pyrolysis of CO was also changed by applying TCOs as the feedstock for the pyrolysis. As shown in Figure 4(a), the content of CO and CO₂ were decreased together with the increase of light hydrocarbons (C₁~C₄) from the pyrolysis of TCO (280-1) torrefied at 280 °C during 1 hour. The bio-oil

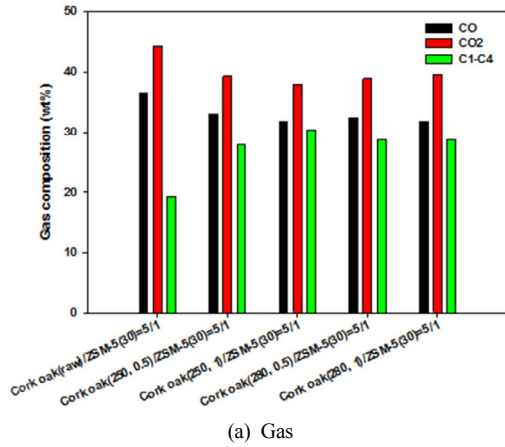
obtained from the pyrolysis of TCO (280-0.5) and TCO (280-1) had the higher content of phenolics and levoglucosan than those of CO. Meanwhile, the contents of phenolics in the bio-oil obtained from TCO (250-0.5) and TCO (250-1) were lower than those obtained from CO. This can suggest that the relative content of lignin also can be decreased when low temperature 250 °C was applied as torrefaction temperature. Although partial amount of lignin is also decomposed at 280 °C, most of hemicellulose is eliminated the torrefaction at 280 °C (Figure 2). Therefore, the relative contents of cellulose and lignin in TCOs torrefied at 280 °C are increased and the contents of their typical pyrolyzates, such as levoglucosan and phenolics, are increased.

3.3. Catalytic pyrolysis of CO and TCOs

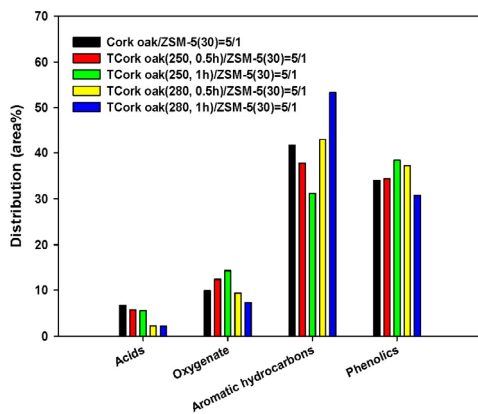
Figure 5 shows the yields of gas, oil, char, and coke obtained from the ex-situ catalytic pyrolysis of CO and TCOs over HZSM-5 at 530 °C. The yield of char was gradually increased together with the decrease of oil by applying the higher torrefaction temperature and time prior to their pyrolysis. This tendency is coincide with the non-catalytic pyrolysis results (Figure 3).

Compared to non-catalytic pyrolysis, Figure 4(a), catalytic pyrolysis of CO and TCOs over HZSM-5 produced much larger amount of light hydrocarbons by the additional cracking over HZSM-5, as shown in Figure 6(a). The contents of aromatic hydrocarbons were also increased together with the decrease contents of acids and phenolics, as shown in Figure 6(b). The oxygen containing pyrolyzates of biomass, such as acids, levoglucosan, and phenolics, can be converted to light hydrocarbons and aromatic hydrocarbons by the additional cracking, dehydration, decarboxylation, decarbonylation, and aromatization reaction over HZSM-5[18]. The product distributions in gas and oil obtained from the catalytic pyrolysis of different TCOs were also different depends on the torrefaction condition. Among various TCOs, TCO (280-1) produced the highest quality oil having the highest content of aromatic hydrocarbons. This can suggest that the torrefaction of CO can be helpful for the production of high quality oil when proper temperature (280 °C) and time (1 hour) were applied as torrefaction condition.

The chemical distributions of phenolics in the oil produced from the catalytic pyrolysis of CO and TCOs were shown in Figure 7. TCOs ex-



(a) Gas



(b) Oil

Figure 6. Product distribution of gas and oil obtained from the catalytic pyrolysis of CO and TCOs over HZSM-5 at 530 °C.

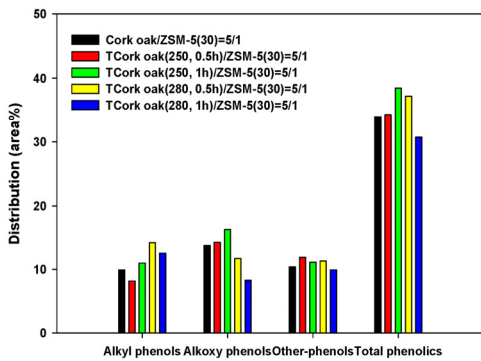


Figure 7. Detailed product distributions of phenolics in the bio-oil obtained from the catalytic pyrolysis of CO and TCOs over HZSM-5 at 530 °C.

cept TCO (250-0.5) produced the oil having the higher content of alkyl phenols than CO because biomass torrefaction can increase the demethoxylation and the cleavage of aryl ether linkages of lignin[14-15].

The yields of gas, oil, char and coke (Figure 8) and product distributions of gas and oil (Figure 9) were also differentiated by increasing the catalyst bed temperature from 530 °C to 600 °C. By increasing the catalyst bed temperature, the yield of gas was increased together

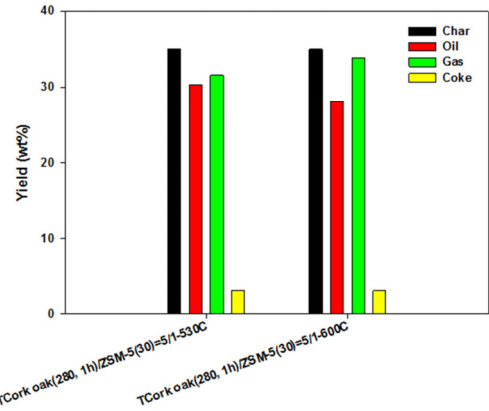
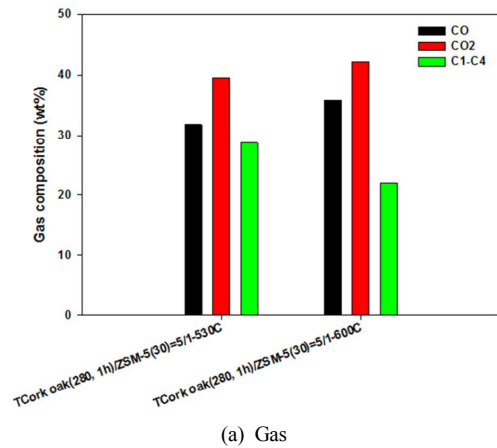
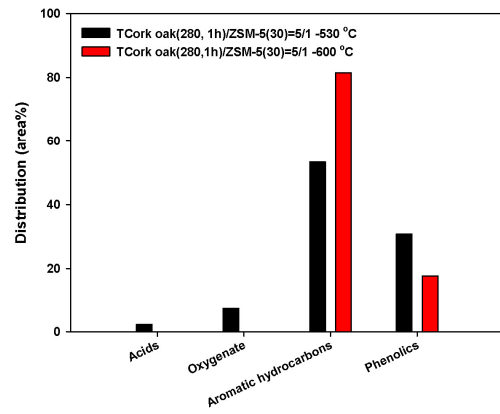


Figure 8. The yields of gas, oil, char, and coke obtained from the catalytic pyrolysis of TCO (280-1) over HZSM-5 at 530 and 600 °C.



(a) Gas



(b) Oil

Figure 9. Detailed product distributions of gas and oil obtained from the catalytic pyrolysis of TCO (280-1) over HZSM-5 at 530oC and 600 °C.

with the decrease of oil because the catalytic cracking and upgrading efficiency can be increased at the higher temperature. The contents of CO and CO₂ in gas were increased by increasing the catalyst bed temperature, meanwhile, that of light hydrocarbons (C1~C4) was decreased, as shown in Figure 9(a). This can suggest that the Diels-Alder reaction between the light hydrocarbons can be increased by applying

the higher catalyst bed temperature and increase the contents of aromatic hydrocarbons, as shown in Figure 9(b).

4. Conclusion

In this study, the effect of torrefaction on thermal and catalytic pyrolysis of CO was investigated to increase the amount of value added chemicals in the product oil. By applying the torrefaction of CO at higher temperature and time, the content of C and fixed carbon were increased together with the decrease of O and volatile contents due to the elimination of hemicellulose. Pyrolysis product of TCO had the higher contents of levoglucosan and phenolics due to the relatively high contents of cellulose and lignin in TCOs torrefied at 280 °C. By the use of HZSM-5 as the ex-situ catalytic pyrolysis of CO and TCOs, the yields of aromatic hydrocarbons in product oil were increased due to the additional cracking and upgrading efficiency over HZSM-5. Among CO and various TCOs torrefied at different condition, TCO (280-1) produced the highest quality oil having the highest content of aromatic hydrocarbons. Increased catalyst bed temperature also increased the content of aromatic hydrocarbon in oil via the improved Diels-Alder reaction over HZSM-5.

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